Derivations of the Young-Laplace equation

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Abstract

The classical Young-Laplace equation relates capillary pressure to surface tension and the principal radii of curvature of the interface between two fluids. It is here derived along two main approaches to describe properties of space curves and smooth surfaces: (1) by differential geometry and (2) linear algebra, in combination with considerations of (a) force equilibrium, and (b) minimization of surface energy.

Introduction

The Young-Laplace equation (Young, 1805; Laplace, 1806)

$$p_c = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \tag{1}$$

gives an expression for the capillary pressure p_c, i.e., the pressure difference over an interface between two fluids in terms of the surface tension σ and the principal radii of curvature, R_1 and R_2. This expression is often encountered in the literature covering the concepts of capillary pressure and wettability since it is quite general.

The expression in parenthesis in Eq. 1 is a geometry factor. At equilibrium, each point on the interface has the same geometry factor.

It will be shown that this simple expression reflects the fact that for arbitrary, *smooth* surfaces and curves (Shifrin, 2013), the curvature at any point may be defined by assigning two radii of curvature, R_1 and R_2, in two *normal planes* that cut the interface along two *principal curvature sections*. These two normal planes

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are also normal to each other and their line of intersection is the surface normal at the chosen point. Also, the curvature of an arbitrary normal section may be expressed in terms of the principal curvatures.

With sufficient knowledge of the mathematical properties of surfaces, the Young-Laplace equation may easily be derived either by the principle of minimum energy or by requiring a force balance.

The properties of surfaces necessary to derive the Young-Laplace equation may be found explicitly by differential geometry or more indirectly by linear algebra. The combination of these two approaches gives insight into the properties of smooth space surfaces that are required for the simple form of Young-Laplace equation.

Space curves by differential geometry

Most of this section follows the exposition of space curves in the textbook by Tambs Lyche (1962).

Let **r** denote the radius vector from the origin of the Cartesian coordinate system (x, y, z) with unit vectors $(\mathbf{i}, \mathbf{j}, \mathbf{k})$. A surface S may be defined by the vector equation

$$\mathbf{r} = \mathbf{f}(u, v) = \varphi(u, v)\mathbf{i} + \psi(u, v)\mathbf{j} + \chi(u, v)\mathbf{k}, \tag{2}$$

or in parameter form

$$x = \varphi(u, v), \quad y = \psi(u, v), \quad z = \chi(u, v), \tag{3}$$

where φ, ψ and χ are functions of the two parameters u and v. If the two first equations in Eq. 3 are solved for u and v and substituted in the third equation, we get z expressed as a function of x and y, the usual way to represent a surface. However, the parameter form is a very useful representation of a surface to describe curvature characteristics.

If we set $u = u(t)$ and $v = v(t)$ we get the vector equation $\mathbf{r} = \mathbf{f}(t)$ for a space curve on the surface, or in parameter form:

$$x = \varphi(t), \quad y = \psi(t), \quad z = \chi(t),$$

where t is a parameter. By assumption, all functions are twice differentiable with continuous second order derivatives. A curve or surface represented by functions fulfilling this requirement is said to be *smooth*.

Definitions

Arc Length. If $\mathbf{f}(t)$ is differentiable with continuous derivative in the interval $[a,b]$, then the arc length $\mathcal{L}$ is defined by

$$\mathcal{L} = \int_a^b |\dot{\mathbf{f}}(t)| dt,$$

where the dot denotes differentiation with respect to t. If $t \in [a, b]$ and we set $s = \int_a^t |\dot{\mathbf{f}}(t)| dt$, we get the arc differential $ds = |\dot{\mathbf{f}}(t)| dt = \pm |d\mathbf{r}|$. Then s is a continuous function of t that increases from 0 to $\mathcal{L}$ when t increases from a to b. Instead of t, we can use s as a parameter to represent the curve. By this *arc length* form, many formulas are especially simple, e.g., $|\mathbf{r}'| = |d\mathbf{r}/ds| = 1$.

Tangent to a Curve. The vector $\mathbf{t} = d\mathbf{r}/ds = \mathbf{r}'$ is defined as the *tangent vector* of the space curve $\mathbf{r} = \mathbf{f}(t)$. Since $|\mathbf{t}| = 1$, $\mathbf{t}$ is a unity vector along the tangent of the curve.

Curvature. The *curvature* K of a curve is defined by $K = |d\mathbf{t}/ds| = |d^2\mathbf{r}/ds^2| = |\mathbf{r}''|$, or simply $K = |\mathbf{f}''(s)|$, the curve being on the arc length form.

Radius of Curvature. The radius of curvature R of a space curve C is defined by $R = 1/K$.

Principal Normal to a Curve. The *principal normal* $\mathbf{h}$ of a curve is defined by $\mathbf{h} = \mathbf{r}''/|\mathbf{r}''| = \mathbf{r}''/K$. Since $\mathbf{r}'^2 = 1$ it follows that $\mathbf{r}' \cdot \mathbf{r}'' = 0$, and hence $\mathbf{h}$ is normal to $\mathbf{t}$ (and the curve).

Normal of a Surface. The *surface normal* $\mathbf{n}$ to a surface at a point is defined by $\mathbf{n} = \mathbf{r}_u \times \mathbf{r}_v / |\mathbf{r}_u \times \mathbf{r}_v|$. Here $\mathbf{r}_u$ and $\mathbf{r}_v$ denotes partial derivatives of $\mathbf{r}$ with respect to u and v, cf. Eq. 2. The total differential $d\mathbf{r}$ is given by

$$d\mathbf{r} = \mathbf{r}_u du + \mathbf{r}_v dv,$$

and for the space curve on the surface, $u = u(t)$ and $v = v(t)$. From the definition of $\mathbf{t}$, $d\mathbf{r}$ is along $\mathbf{t}$, and it is easily seen that $d\mathbf{r} \cdot \mathbf{n} = 0$. That is, $\mathbf{n}$ is normal to all curves on the surface drawn through the selected point.

Normal Plane and Normal Section. A plane through the normal to a surface, i.e., the normal is lying in the plane, is called a *normal plane* The cut between a normal plane and the surface is a curve on the surface and is called a *normal section*.

Curvature of a Normal Section

Again, let $\mathbf{r} = \mathbf{f}(u, v)$ a surface S and $\mathbf{r} = \mathbf{f}(u(t), v(t))$ a space curve C on S. From the definitions, we have $K\mathbf{h} = d\mathbf{t}/ds$. Multiplying by $\mathbf{n}$ gives

$$\frac{d\mathbf{t}}{ds}\mathbf{n} = K\cos\theta,$$

where θ is the angle between the principal normal to C and the surface normal at the chosen point P, Fig. 1.

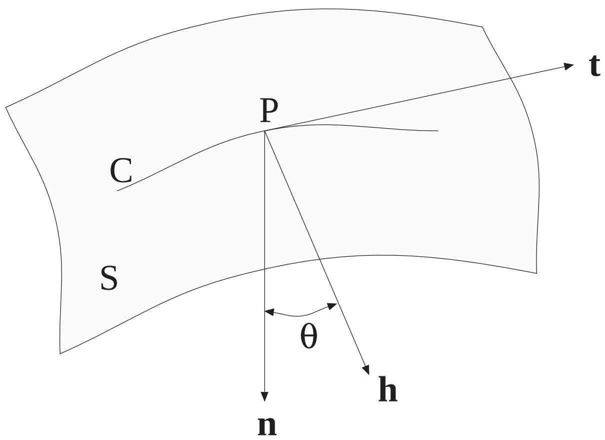

Figure 1: Surface S, curve C through point P, **t** tangent to the curve, **n** surface normal, and **h** principal normal to the curve.

Since $\mathbf{n} \cdot \mathbf{t} = 0$, we get by differentiation

$$\mathbf{n}\frac{d\mathbf{t}}{ds} + \frac{d\mathbf{n}}{ds}\mathbf{t} = 0,$$

and thereby

$$K = -\frac{1}{\cos\theta}\frac{d\mathbf{n}}{ds}\mathbf{t} = -\frac{1}{\cos\theta}\frac{d\mathbf{n} \cdot d\mathbf{r}}{ds^2}.$$

From the definition of $\mathbf{n}$, we have $\mathbf{r}_u\mathbf{n} = 0$, $\mathbf{r}_v\mathbf{n} = 0$. Differentiating with respect to u and v, we get

$$\begin{aligned} \mathbf{r}_u\mathbf{n}_u + \mathbf{r}_{uu}\mathbf{n} &= 0, \qquad & \mathbf{r}_v\mathbf{n}_u + \mathbf{r}_{uv}\mathbf{n} &= 0, \\ \mathbf{r}_u\mathbf{n}_v + \mathbf{r}_{uv}\mathbf{n} &= 0, \qquad & \mathbf{r}_v\mathbf{n}_v + \mathbf{r}_{vv}\mathbf{n} &= 0. \end{aligned}$$

Since

$$d\mathbf{n} = \mathbf{n}_u du + \mathbf{n}_v dv, \quad d\mathbf{r} = \mathbf{r}_u du + \mathbf{r}_v dv,$$

we have

$$\begin{aligned} d\mathbf{n}\cdot d\mathbf{r} &= \mathbf{r}_u\mathbf{n}_u du^2 + (\mathbf{r}_u\mathbf{n}_v + \mathbf{r}_v\mathbf{n}_u) du\,dv + \mathbf{r}_v\mathbf{n}_v dv^2 \\ &= -(\mathbf{r}_{uu}\mathbf{n}\,du^2 + 2\mathbf{r}_{uv}\mathbf{n}\,du\,dv + \mathbf{r}_{vv}\mathbf{n}\,dv^2), \end{aligned}$$

and we get

$$K = \frac{1}{\cos\theta}\frac{L\,du^2 + 2M\,du\,dv + N\,dv^2}{E\,du^2 + 2F\,du\,dv + G\,dv^2}, \tag{4}$$

when

$$\begin{aligned} ds^2 &= d\mathbf{r}^2 = (\mathbf{r}_u du + \mathbf{r}_v dv)^2 \\ &= \mathbf{r}_u^2 du^2 + 2\mathbf{r}_u\mathbf{r}_v du dv + \mathbf{r}_v^2 dv^2 \end{aligned}$$

and

$$\begin{array}{lll} E = \mathbf{r}_u^2, & F = \mathbf{r}_u\mathbf{r}_v, & G = \mathbf{r}_v^2, \\ L = \mathbf{r}_{uu}\mathbf{n}, & M = \mathbf{r}_{uv}\mathbf{n}, & N = \mathbf{r}_{vv}\mathbf{n}. \end{array} \tag{5}$$

We note that the quantities E, F, G, L, M, N only depend on properties of the surface S with no reference to the space curve C on the surface. For all curves C that start out from point P in the same direction, determined by the ratio $dv : du$, the angel θ is the same according to Eq. 4. Conversely, all space curves through P with the same **t** and **h** has the same curvature at P.

If we choose $\theta = 0$, K is the curvature of a normal section, i.e., the principal normal of the curve coincides with the normal to the surface,

$$K = \frac{L\,du^2 + 2M\,du\,dv + N\,dv^2}{E\,du^2 + 2F\,du\,dv + G\,dv^2}. \tag{6}$$

Principal Curvature Sections

If K is known, Eq. 6 is a quadratic equation for the ratio $dv : du$, and may be written

$$(L - EK)\,du^2 + 2(M - FK)\,du\,dv + (N - GK)\,dv^2 = 0. \tag{7}$$

If this equation has two distinct roots, there will be two normal sections with curvature K. If it has only one root, there exist only one normal section with the given curvature, and if there are no roots, no normal section exists with curvature K. To discern these alternatives, we consider the expression

$$(M - FK)^2 - (L - EK)(N - GK)$$

that is under the square root sign when solving Eq. 7. This expression is generally equal to zero for two values of K, the *principal curvatures* K_1 and K_2. The corresponding normal sections are called the *principal curvature sections*.

After simplifying the last expression, we have to investigate the roots of

$$(EG - F^2)K^2 - (EN - 2FM + GL)K + (LN - M^2) = 0. \tag{8}$$

Solving this equation we have to find the square root of

$$(EN - 2FM + GL)^2 - 4(EG - F^2)(LN - M^2).$$

As will be shown, this expression is never negative. Let us assume chosen values for E, F, G, L, N such that the last expression is a function of M, denoted by $\varphi(M)$. It is a polynomial of second degree with the derivative

$$\varphi'(M) = -4F(EN - 2FM + GL) + 8(EG - F^2)M,$$

and $\varphi'(M) = 0$ for $M = M_1 = F(EN + GL)/2EG$. Then $\varphi''(M) = 8EG > 0$, from the definition of E and G, i.e. $\varphi(M)$ has a minimum at $M = M_1$, and after some calculation

$$\varphi(M_1) = \frac{(EG - F^2)(EN - GL)^2}{EG} \geq 0,$$

since $EG - F^2 = \mathbf{r}_u^2\mathbf{r}_v^2 - (\mathbf{r}_u\mathbf{r}_v)^2 = (\mathbf{r}_u \times \mathbf{r}_v)^2 \geq 0$. Actually, we will assume that $EG - F^2 > 0$ since otherwise $\mathbf{r}_u$ or $\mathbf{r}_v$ is the null vector or they are parallel. Then $\varphi(M)$ can only be zero if $EN = GL$ and $M = M_1$, i.e. $GM = FN$. We then have

$$\frac{L}{E} = \frac{N}{G} = \frac{M}{F},$$

and from Eq. 6 the curvature K is independent of du and dv and equal to L/E. A point where the curvature is the same for all normal sections is called a *umbilical point* of the surface.

For a point P on the surface that is not a umbilical point, Eq. 8 will have two distinct roots, K_1 and K_2, as postulated above.

Principal Curvature Sections are Orthogonal

Substitution of $K = K_1$ or $K = K_2$ into Eq. 7 results in a quadratic expression of the general form $(Adu + Bdv)^2$, since the equation has single roots for these values of K. Its derivative with respect to dv then has to be zero for the same values of K, that is

$$(M - FK)du + (N - GK)dv = 0,$$

or

$$K = \frac{Mdu + Ndv}{Fdu + Gdv}.$$

Substituting this expression into Eq. 7, we get

$$(EM - FL)du^2 + (EN - GL)dudv + (FN - GM)dv^2 = 0.$$

From this equation we get the two directions $dv_1 : du_1$ and $dv_2 : du_2$ (or the inverted ratios if $FN - GM = 0$), for the two principal curvature sections. Using rules for the sum and product of the roots of a quadratic equation, we get

$$\frac{dv_1}{du_1} + \frac{dv_2}{du_2} = -\frac{EN - GL}{FN - GM}, \quad \frac{dv_1}{du_1}\frac{dv_2}{du_2} = \frac{EM - FL}{FN - GM}.$$

We also have

$$d\mathbf{r}_1 = \mathbf{r}_u du_1 + \mathbf{r}_v dv_1, \quad d\mathbf{r}_2 = \mathbf{r}_u du_2 + \mathbf{r}_v dv_2,$$

and hence

$$\begin{aligned}
d\mathbf{r}_1 \cdot d\mathbf{r}_2 &= \mathbf{r}_u^2 du_1 du_2 + \mathbf{r}_u \mathbf{r}_v (du_1 dv_2 + du_2 dv_1) + \mathbf{r}_v^2 dv_1 dv_2 \\
&= \left[E + F\left(\frac{dv_1}{du_1} + \frac{dv_2}{du_2}\right) + G\frac{dv_1}{du_1}\frac{dv_2}{du_2}\right] du_1 du_2 \\
&= \left[E - F\frac{EN - GL}{FN - GM} + G\frac{EM - FL}{FN - GM}\right] du_1 du_2 \\
&= \frac{E(FN - GM) - F(EN - GL) + G(EM - FL)}{FN - GM} du_1 du_2 \\
&= 0,
\end{aligned}$$

i.e. the principal curvature sections are orthogonal. (One can easily show that this is the case also for $FN - GM = 0$).

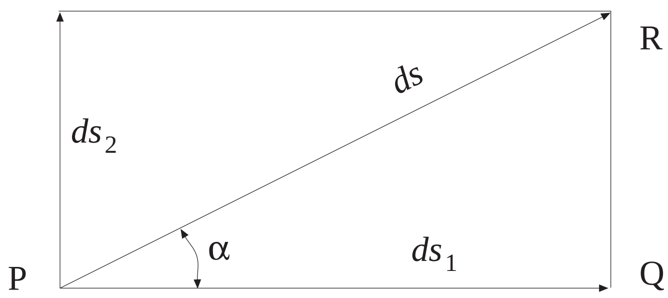

Figure 2: Arc differentials along a normal section and the two principal curvature sections.

A Theorem of Euler

A theorem of Euler (Weatherburn, 1947) states that the curvature of an arbitrary normal section may be expressed by the curvatures of the principal sections. Let ds_1 and ds_2 be the arc differentials of the two principal sections and ds the arc differential in a normal section at an angle α with ds_1, Fig. 2.

Generally, if $\Phi(u, v)$ is a function of u and v, we have

$$\Phi(\mathrm{R}) - \Phi(\mathrm{P}) = \Phi(\mathrm{R}) - \Phi(\mathrm{Q}) + \Phi(\mathrm{Q}) - \Phi(\mathrm{P}),$$

or

$$\frac{\Phi(\mathrm{R}) - \Phi(\mathrm{P})}{ds} = \frac{\Phi(\mathrm{R}) - \Phi(\mathrm{Q})}{ds_1}\frac{ds_1}{ds} + \frac{\Phi(\mathrm{Q}) - \Phi(\mathrm{P})}{ds_2}\frac{ds_2}{ds},$$

and letting ds_1 and ds_2 approach zero,

$$\frac{d\Phi}{ds} = \frac{d\Phi}{ds_1}\frac{ds_1}{ds} + \frac{d\Phi}{ds_2}\frac{ds_2}{ds} = \frac{d\Phi}{ds_1}\cos\alpha + \frac{d\Phi}{ds_2}\sin\alpha.$$

We now apply this general expression to **r** and **n** and get

$$\begin{aligned} \mathbf{t} \;=\; & \frac{d\mathbf{r}}{ds} = \mathbf{t}_1 \cos\alpha + \mathbf{t}_2 \sin\alpha \\ & \frac{d\mathbf{n}}{ds} = \frac{d\mathbf{n}}{ds_1}\cos\alpha + \frac{d\mathbf{n}}{ds_2}\sin\alpha, \end{aligned}$$

and by scalar multiplying these two expressions,

$$\begin{aligned} -K &= \mathbf{t}\frac{d\mathbf{n}}{ds} \\ &= \mathbf{t}_1\frac{d\mathbf{n}}{ds_1}\cdot\cos^2\alpha + \left(\mathbf{t}_1\frac{d\mathbf{n}}{ds_2} + \mathbf{t}_2\frac{d\mathbf{n}}{ds_1}\right)\sin\alpha\cos\alpha + \mathbf{t}_2\frac{d\mathbf{n}}{ds_2}\cdot\sin^2\alpha \\ &= -K_1\cos^2\alpha - K_2\sin^2\alpha + \left(\mathbf{t}_1\frac{d\mathbf{n}}{ds_2} + \mathbf{t}_2\frac{d\mathbf{n}}{ds_1}\right)\sin\alpha\cos\alpha. \end{aligned}$$

Since $\mathbf{n} \cdot \mathbf{t}_1 = \mathbf{n} \cdot \mathbf{t}_2 = 0$, we get

$$\mathbf{t}_1 \frac{d\mathbf{n}}{ds_2} + \mathbf{n} \frac{\mathbf{t}_1}{ds_2} = 0, \quad \mathbf{t}_2 \frac{d\mathbf{n}}{ds_1} + \mathbf{n} \frac{\mathbf{t}_2}{ds_1} = 0.$$

The curves C_1 and C_2 are embedded in two orthogonal planes, $\mathbf{t}_1 \cdot \mathbf{t}_2 = 0$, and $\mathbf{t}_1$ is independent of s_2. Therefore $d\mathbf{t}_1/ds_2 = 0$ and likewise $d\mathbf{t}_2/ds_1 = 0$, and we get Euler's result

$$K = K_1 \cos^2 \alpha + K_2 \sin^2 \alpha. \tag{9}$$

Let us now choose another normal section at an angle $\alpha + \pi/2$ with ds_1 and denote the corresponding arc differential by $ds_\perp$ since it is at an angle $\pi/2$ with ds. For the corresponding curvature $K_\perp$ we get from Eq. 9

$$\begin{aligned} K_\perp &= K_1 \cos^2(\alpha + \pi/2) + K_2 \sin^2(\alpha + \pi/2) \\ &= K_1 \sin^2 \alpha + K_2 \cos^2 \alpha. \end{aligned}$$

By summation, we the get

$$K + K_\perp = K_1 + K_2, \tag{10}$$

that is, the sum of the curvatures of two orthogonal normal sections is constant, equal to the sum of the curvatures of the principal sections.

The Young-Laplace Equation

The Young-Laplace equation may be derived either by minimization of energy or by summing all forces to zero. We will do both here although the concept of force in connection with surface tension may be somewhat obscure. The force approach follows the derivation of Defay and Prigogine (1966) and the energy approach is taken from the book by Landau and Lifshitz (1987). In both cases it is assumed that the interface is without thickness and that the interfacial tension is constant.

Force Balance

Consider a point P on the surface, Fig. 3, and draw a curve at a constant distance ρ from P. This curve forms the boundary of a cap for which we shall find the equilibrium condition as ρ tends to zero.

Through P we draw the two principal curvature sections AB and CD on the surface. Their radii of curvature at P are R_1 and R_2. At the point A, an element δl

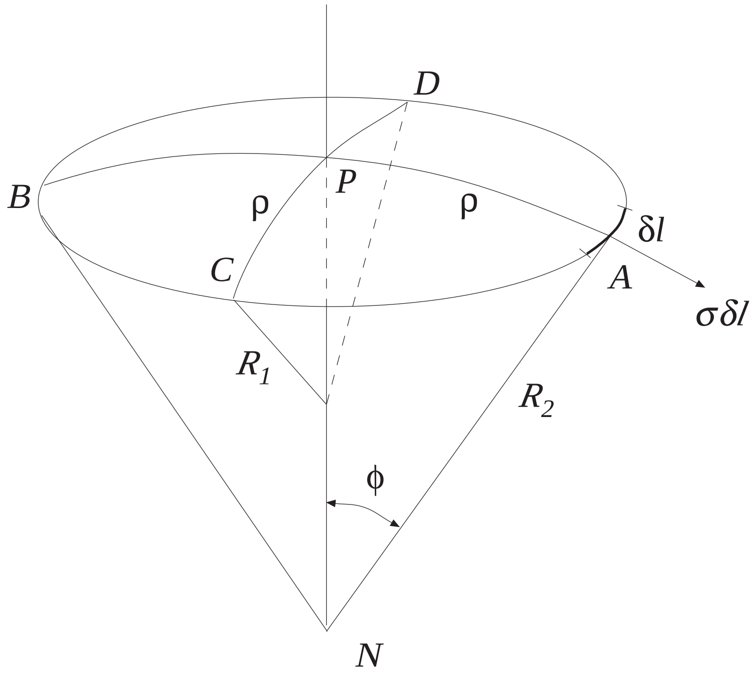

Figure 3: Equilibrium of a nonspherical cap.

of the boundary line is subjected to a force $\sigma\delta l$ whose projection along the normal PN is

$$\sigma\delta l \sin\phi \simeq \sigma\phi\delta l = \sigma\frac{\rho}{R_2}\delta l,$$

since ϕ by assumption is small.

If we consider four elements δl of the periphery at A, B, C, and D, they will contribute with a force

$$2\rho\sigma\delta l\left(\frac{1}{R_1}+\frac{1}{R_2}\right).$$

Since this expression by Euler's theorem, Eq. 10, is independent of the choice of AB and CD, it can be integrated around the circumference. Since four orthogonal elements are considered, the integration is made over one quarter of a revolution to give

$$\pi\rho^2\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right).$$

The force on the surface element caused by the pressure difference over the surface is given by $(p_1-p_2)\pi\rho^2$, and equating the last two expressions Laplace's equation follows.

Minimum Energy

Let the surface of separation undergo an infinitesimal displacement. At each point of the undisplaced surface we draw the normal. The length of the segment of the normal lying between the points where it intersects the displaced and undisplaced surfaces is denoted by $\delta\zeta$. Then a volume element between the two sufaces is $\delta\zeta df$, where df is a surface element. Let p_1 and p_2 be the pressures in the two media, and let $\delta\zeta$ be positive if the displacement of the surface is towards medium 2 (say). Then the work necessary to bring about the change in volume is

$$\int(-p_1 + p_2)\delta\zeta df.$$

The total work δW in displacing the surface is obtained by adding to this the work connected with the change in area of the surface. This part of the work is proportional to the change δf in area of the surface, and is $\sigma\delta f$, where σ is the surface tension. Thus the total work is

$$\delta W = -\int(p_1 - p_2)\delta\zeta df + \sigma\delta f. \tag{11}$$

The condition for thermodynamical equilibrium is, of course, that δW be zero.

Next, let R_1 and R_2 be the principal radii of curvature at a given point of the surface. We set R_1 and R_2 as positive if they are drawn into medium 1. Then the elements of length (the arc differentials) ds_1 and ds_2 on the surface in its principal curvature sections are increased to $(R_1 + \delta\zeta)ds_1/R_1$ and $(R_2 + \delta\zeta)ds_2/R_2$ when the angles ds_1/R_1 and ds_2/R_2 remain constant, i.e., an expansion normal to the surface (ds_1 is the arc length of a circle with radius R_1, and correspondingly for ds_2). Hence the surface element $df = ds_1 ds_2$ becomes, after displacement,

$$ds_1(1 + \delta\zeta/R_1)ds_2(1 + \delta\zeta/R_2) \cong ds_1 ds_2(1 + \delta\zeta/R_1 + \delta\zeta/R_2),$$

i.e. it changes by $\delta\zeta df(1/R_1 + 1/R_2)$. Hence we see that the total change in area of the surface of separation is

$$\delta f = \int \delta\zeta \left(\frac{1}{R_1} + \frac{1}{R_2}\right) df. \tag{12}$$

Substituting these expressions in Eq. 11 and equating to zero, we obtain the equilibrium condition in the form

$$\int \delta\zeta \left\{(p_1 - p_2) - \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right\} df = 0.$$

This condition must hold for every infinitesimal displacement of the surface, i.e. for all $\delta\zeta$. Hence the expression in braces must be identically equal to zero and Young-Laplace's equation follows.

Space curves by linear algebra

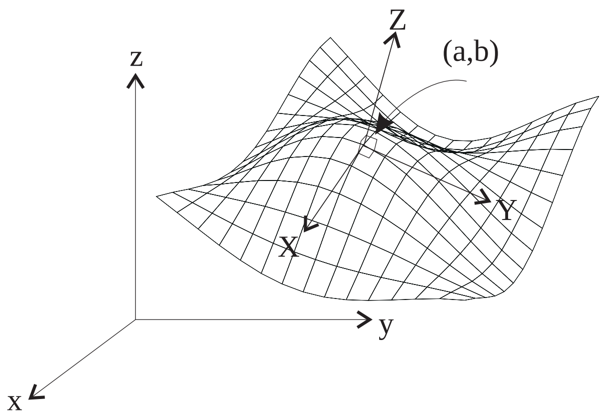

Figure 4: Surface in space.

We assume the space surface defined by $z = f(x, y)$ to be *smooth* (Shifrin, 2013). A Taylor expansion around a point (a, b) gives an approximation to the surface around (a, b),

$$f(x, y) = f(a, b) + \frac{\partial f(a, b)}{\partial x}(x - a) + \frac{\partial f(a, b)}{\partial y}(y - b) + \frac{1}{2!}\left[\frac{\partial^2 f(a, b)}{\partial x^2}(x - a)^2 + \frac{\partial^2 f(a, b)}{\partial y^2}(y - b)^2 + \frac{\partial^2 f(a, b)}{\partial x \partial y}(x - a)(y - b) + \frac{\partial^2 f(a, b)}{\partial y \partial x}(y - b)(x - a)\right] + \cdots. \quad (13)$$

A new coordinate system (XYZ) is now introduced with origin in (a, b) and the (XY) plane defined as the tangent plane to the surface at (a, b). This gives

$$\begin{aligned} f(0, 0) &= 0, \\ \frac{\partial f(0, 0)}{\partial X} &= 0, \end{aligned} \quad (14)$$

$$\frac{\partial f(0,0)}{\partial Y} \;=\; 0.$$

Since the surface is smooth, the order of differentiation is arbitrary, and the crossterms may be added to render

$$\begin{aligned} Z = f(X,Y) &\approx \frac{1}{2!}\left[\frac{\partial^2 f(0,0)}{\partial X^2}X^2 + \frac{\partial^2 f(0,0)}{\partial Y^2}Y^2 + 2\frac{\partial^2 f(0,0)}{\partial X \partial Y}XY\right], \\ &= \frac{1}{2}\left[f_{XX}X^2 + f_{YY}Y^2 + 2 f_{XY}XY\right]. \end{aligned}$$

This may be reformulated as the matrix product

$$f(X,Y) \approx \frac{1}{2}\begin{pmatrix} X & Y \end{pmatrix}\begin{pmatrix} f_{XX} & f_{XY} \\ f_{XY} & f_{YY} \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix}. \tag{15}$$

The 2×2 matrix in Eq. 15 formed by the partial derivatives of f is symmetrical, the matrix can be diagonalized with orthogonal eigenvectors (Howard, 1984), and the surface may be approximated by the matrix product

$$\begin{aligned} f(X,Y) \approx g(\xi,\eta) &= \frac{1}{2}\begin{pmatrix} \xi & \eta \end{pmatrix}\begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix}\begin{pmatrix} \xi \\ \eta \end{pmatrix}, \\ &= \frac{1}{2}\alpha\xi^2 + \frac{1}{2}\beta\eta^2, \end{aligned} \tag{16}$$

Here ξ and η are the coordinates along the new unit vectors and α and β the corresponding eigenvalues. This is equivalent to a rotation of the tangent plane around the Z-axis with the two new unit vectors $(1 \quad 0)^t$ and $(0 \quad 1)^t$ in the $(\xi\eta)$-plane.

In the $(Z\xi)$-plane ($\eta = 0$), the function $g(\xi,0)$ in Eq. 16 will form the parabola

$$Z = g(\xi,0) = \frac{1}{2}\alpha\xi^2. \tag{17}$$

Approximating the parabola with a circle of radius R_α, we get

$$\begin{aligned} \xi^2 + (Z - R_\alpha)^2 &= R_\alpha^2, \\ \xi^2 + Z^2 - 2ZR_\alpha + R_\alpha^2 &= R_\alpha^2, \\ \xi^2 + Z^2 - 2ZR_\alpha &= 0, \end{aligned} \tag{18}$$

and solved with respect to Z,

$$
\begin{aligned}
Z &= R_\alpha \pm \sqrt{R_\alpha^2 - \xi^2}, \\
&= R_\alpha (1 \pm \sqrt{1 - \frac{\xi^2}{R_\alpha^2}}), \\
&= R_\alpha (1 \pm [1 + \frac{\xi^2}{2R_\alpha^2} - \ldots]).
\end{aligned}
$$

Selecting the minus sign and deleting higher order terms, we arrive a the simple expresson

$$
Z \approx \frac{\xi^2}{2R_\alpha}. \tag{19}
$$

By comparing Eq. 17 and Eq. 19 we find

$$
Z = \frac{\alpha \xi^2}{2} = \frac{\xi^2}{2R_\alpha},
$$

and

$$
R_\alpha = \frac{1}{\alpha}. \tag{20}
$$

The curvature κ of a space curve at a point [Reference to part I definitions] is defined as the inverse of the radius of curvature at the point. The curvature of the parabola $Z = g(\xi, 0)$ is therefore

$$
\kappa = \alpha = \frac{1}{R_\alpha}.
$$

Considering instead the $(Z\eta)$-plane ($\xi = 0$), the curvature of the parabola $Z = g(0, \eta)$ is given by

$$
\kappa = \beta = \frac{1}{R_\beta}.
$$

A arbitrary plane normal to the tangent plane at the point (a, b) [Reference to part I definitions] will cut the tangent plane $(\xi\eta)$ along a straight line $l : \xi = K\eta$ where K is a constant as shown i Fig. 5 The distance λ between the point (a, b)

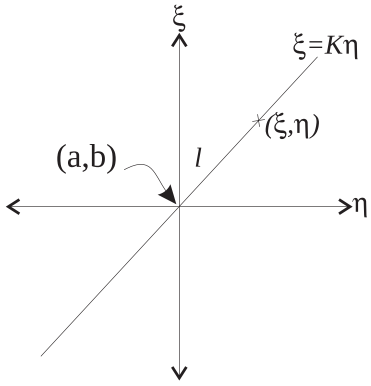

Figure 5: Arbitrary line l through point (a, b) in the tangent plane.

and a point (ξ, η) on l may then be expressed by

$$\begin{aligned} \lambda^2 &= \xi^2 + \eta^2, \\ &= K^2\eta^2 + \eta^2, \\ &= \left(K^2 + 1\right)\eta^2. \end{aligned} \tag{21}$$

Solved with respect to η^2 we get

$$\eta^2 = \frac{\lambda^2}{K^2 + 1}. \tag{22}$$

The cut of the normal plane and the surface $f(\xi, \eta)$ is then

$$\begin{aligned} f(\xi, \eta) &= \frac{1}{2}\alpha\xi^2 + \frac{1}{2}\beta\eta^2, \\ &= \frac{1}{2}\alpha K^2\eta^2 + \frac{1}{2}\beta\eta^2, \\ &= \frac{1}{2}\alpha\left(\frac{K^2\lambda^2}{K^2 + 1}\right) + \frac{1}{2}\beta\left(\frac{\lambda^2}{K^2 + 1}\right), \\ &= \frac{1}{2}\left[\frac{K^2}{K^2 + 1}\alpha + \frac{1}{K^2 + 1}\beta\right]\lambda^2. \end{aligned} \tag{23}$$

The curvature of the space curve defined by the cut between the normal plane touching the surface in (a, b) and the surface $f(\xi, \eta)$ is then, as shown above, given by

$$\kappa_1 = \frac{K^2}{K^2+1}\alpha + \frac{1}{K^2+1}\beta. \tag{24}$$

The expression for the curvature is a weigthed average between α and β. The value of κ_1 lies between α and β, i.e., between the largest and the smallest curvature. Hence the two normal planes containing the space curve with the largest and smallest curvature are normal to each other. These two space curves are called the principal curves.

A normal plane that cuts the tangent plane along the line $\xi = K\eta$ will cut the surface along a curve on the surface, the normal section [Ref to part I] with curvature κ_1. Another normal plane that is normal to the first one will cut the tangent plane in the line $\xi = -\eta/K$ and have a normal section with curvature

$$\kappa_2 = \frac{1}{K^2+1}\alpha + \frac{K^2}{K^2+1}\beta. \tag{25}$$

Adding the two curvatures from Eqs. 24 and 25, vi get

$$\kappa_1 + \kappa_2 = \alpha + \beta. \tag{26}$$

The sum of the curvatures of two normal sections in planes also normal to each other is constant and equal to the sum of the curvatures of the principal curves.

Surface energy and the Young-Laplace equation

We now consider the surface between two phases to be infitesimally displaced by $\delta\zeta$. The volume element between the two surfaces is $\delta\zeta \cdot dS$ where dS is the surface element. Let P_1 and P_2 denote the pressures in the two phases. The work done by the volume change is

$$\delta W_p = \int (-P_1 + P_2)\,\delta\zeta\, dS. \tag{27}$$

The total work of the displacement also includes the work of changing the surface area by δS and is given by

$$\delta W_\sigma = \sigma\delta S, \tag{28}$$

where σ is the surface tension. And the total work is

$$\delta W = \int (P_2 - P_1)\,\delta\zeta\, dS + \sigma\delta S. \tag{29}$$

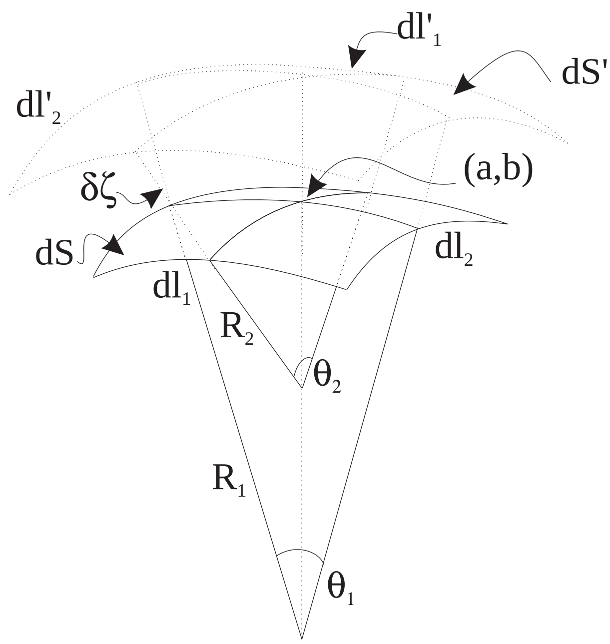

Figure 6: Displaced surface between two phases.

At thermodynamic equilibrium this work is equal to zero.

It remains to express the surface area change δS,

$$\delta S = dS' - dS, \tag{30}$$

in terms of the displacement $\delta\zeta$ and the curvatures of the principal normal sections, $1/R_1$ and $1/R_2$. The surface areas before and after the displacement, dS and dS', respectively, are equal to the product of the length elements along the principal normal sections since, as shown earlier, the normal sections are normal to each other. Then,

$$\begin{aligned} dS &= dl_1 dl_2, \\ dS' &= dl'_1 dl'_2, \end{aligned} \tag{31}$$

where dl_1, dl_2 and dl'_1, dl'_2 are the length elements long the principal normal sections before and after the displacement, respectively. The length elements dl_1 and dl'_1 may be written as

$$\begin{aligned} dl_1 &= R_1\theta_1, \\ dl'_1 &= (R_1 + \delta\zeta)\theta_1, \end{aligned}$$

where θ_1 is the angle shown in Fig. 6. Then

$$\begin{aligned}
\frac{dl_1'}{dl_1} &= \frac{R_1 + \delta\zeta}{R_1} \\
&= 1 + \frac{\delta\zeta}{R_1}.
\end{aligned}$$

Similar expressions are valid for dl_2 and dl_2'. We substitute for dl_1' and dl_2' in Eq. 31 and get

$$\begin{aligned}
dS' &= dl_1' dl_2', \\
&= \left(1 + \frac{\delta\zeta}{R_1}\right) dl_1 \left(1 + \frac{\delta\zeta}{R_2}\right) dl_2, \\
&= dl_1 dl_2 \left(1 + \frac{\delta\zeta}{R_1}\right)\left(1 + \frac{\delta\zeta}{R_2}\right), \\
&= dS\left(1 + \frac{\delta\zeta}{R_1} + \frac{\delta\zeta}{R_2} + \frac{\delta\zeta^2}{R_1 R_2}\right), \\
&\approx dS\left(1 + \frac{\delta\zeta}{R_1} + \frac{\delta\zeta}{R_2}\right), \quad \text{since } \delta\zeta^2 \ll R_1 R_2.
\end{aligned} \tag{32}$$

If this expression is substituted into Eq. 30 we get

$$\begin{aligned}
\delta S &= dS' - dS, \\
&= dS\left(1 + \frac{\delta\zeta}{R_1} + \frac{\delta\zeta}{R_2}\right) - dS, \\
&= dS\left(\frac{\delta\zeta}{R_1} + \frac{\delta\zeta}{R_2}\right).
\end{aligned} \tag{33}$$

This expression is inserted for δS in Eq. 29 to give

$$\begin{aligned}
\delta W &= \int (P_2 - P_1)\,\delta\zeta\, dS + \int \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\delta\zeta\, dS \\
&= \int \left\{-P_c + \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right\}\delta\zeta\, dS, \\
&= 0, \quad \text{for alle} \quad \delta\zeta,
\end{aligned} \tag{34}$$

where $P_c = P_1 - P_2$ is the capillary pressure. Then, according to the fundamental lemma of calculus of variations Papatzacos (1989),

$$-P_c + \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = 0,$$

and rearranged we get

$$P_c = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \tag{35}$$

which is the Young-Laplace equation.

Nomenclature

$[a, b]$	=	interval
$\left.\begin{matrix} E\,F\,G \\ L\,M\,N \end{matrix}\right\}$	=	parameters defined by Eq. 5.
f	=	area, m^2
K	=	curvature, m^{-1}
$\mathcal{L}$	=	arc length, m
dl_1, dl_2	=	length elements, m
dl'_1, dl'_2	=	length elements, m
p	=	pressure, Pa
R	=	radius of curvature, m
R_1, R_2	=	principal radii of curvature, m
s	=	arc length parameter, m
t	=	parameter, dimensionless
u	=	parameter, dimensionless
v	=	parameter, dimensionless
(x, y, z)	=	Cartesian coordinates
W	=	work, J
α	=	angle, radians
δ	=	differential operator
$\delta\zeta$	=	infinitesimal displacement of surfaces, m
σ	=	surface tension, N/m
θ	=	angle, radians
ς	=	length element along normal, m
φ	=	function of (u, v)
ψ	=	function of (u, v)
χ	=	function of (u, v)
ρ	=	radius of cap, m
ϕ	=	angle, radians

Subscripts

c	=	capillary
u	=	partial derivative with respect to u
v	=	partial derivative with respect to v
α	=	constant
Γ	=	adsorption (kg surfactant/kg rock)
γ	=	interfacial tension, N/m

Vectors

$\mathbf{f}$	=	vector function, m
$\mathbf{r}$	=	radius vector, m
$\mathbf{t}$	=	tangent vector, dim.less
$\mathbf{i}, \mathbf{j}, \mathbf{k}$	=	unit vectors, dim.less
$\mathbf{h}$	=	principal normal to a curve, dim.less
$\mathbf{n}$	=	surface normal, dim.less

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